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A STUDY ON ALPHA CASE DEPTH IN Ti-6Al-2Sn-4Zr-2Mo (PREPRINT)

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14. ABSTRACT
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A Study on Alpha Case Depth in Ti-6Al-2Sn-4Zr-2Mo

KEVIN S. McREYNOLDS and SESHACHARYULU TAMIRISAKANDALA

Isothermal oxidation experiments in air were performed on Ti-6Al-2Sn-4Zr-2Mo (Ti-6242) with a bi-modal microstructure in the temperature range 538–649 °C for up to 500 hours and α-case depths were quantified using metallography. Alpha case depth followed a parabolic variation with time. Alpha case depths in excess of 10 μm formed above 538 °C and 100 h exposures. An activation energy of 244 kJ/mol was estimated for diffusion of oxygen in the α phase of Ti-6242.

Keywords: Titanium alloys, static oxidation, alpha case, surface diffusion, activation analysis

The high chemical affinity of titanium to oxygen (indicated by Ti-O bond energy of 2.12 eV, comparable to the Ti-Ti bond energy of 2.56 eV [1]), and the high interstitial solid solubility of oxygen in α-titanium (about 14.5 wt.% or 34 at.% in pure titanium [2]) cause significant oxygen ingression during air exposure at high temperatures resulting in the simultaneous formation of an oxide (TiO_2) scale on the surface and an oxygen-rich α layer underneath the scale, as illustrated in Figure 1. Formation of an oxygen-rich α layer is a result of the oxygen gradient, oxygen migration through the *n*-type anion-defective TiO_2 scale, and the relative ease of interstitial diffusion. This layer is commonly referred to as α-case since it is a continuous, hard, and brittle zone of oxygen stabilized α phase. Alpha case forms during casting [3], processing [4], and elevated temperature exposure in service. Alpha case formed during casting or processing is completely removed via machining or chemical milling [5]. Alpha case formed during service often limits the maximum service temperature of titanium alloys since significant amount of less ductile α-case results in the formation of surface cracks under tensile loading. Incorporation of oxygen leads to anisotropic lattice distortions, thus hindering dislocation mobility and changing the deformation behavior from a wavy to a planar slip mode. The low local ductility and the large slip offsets at the surface can cause low overall ductility or early crack nucleation under

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cyclic loading conditions. The service conditions that affect the oxidation kinetics are environment, temperature, stress, and exposure time. For long-term elevated-temperature applications such as blades, disks, and impellers in gas turbine aero-engines, α-case depth is critically important in addition to creep resistance and strength. For short-term elevated-temperature applications such as thermal protection systems and hot structures that include thin-wall components, rapid degradation across the entire cross-section could occur due to α-case formation. The high temperature application of conventional titanium alloys is therefore limited to a temperature regime below which diffusion rates through the oxide scale are slow enough to prevent excess oxygen content being dissolved in the bulk material, resulting in no significant α-case depth.

While the α-case formation and its deleterious effects on component life are well-known [6], quantitative studies on α-case are scanty. Shamblen and Redden [7] determined the air contamination rates using microhardness traverses and approximated diffusion of oxygen in the α phase of high temperature titanium alloy Ti-6Al-2Sn-4Zr-2Mo (Ti-6242, all compositions are given in weight percent unless noted otherwise) bar stock based on a relationship between oxygen concentration and microhardness. Shenoy et al. [8] studied the oxidation kinetics in Ti-6242 sheet and foil using thermo-gravimetric analysis and estimated the substrate contamination from empirical relations using weight gain and microhardness measurements. Similar studies were performed on other high temperature Ti alloys Ti-5.8Al-4Sn-3.5Zr-0.5Mo-0.7Nb-0.35Si-0.06C (IMI 834) [9] and Ti-6Al-2.7Sn-4Zr-0.4Mo-0.45Si (Ti-1100) [10]. Indirect measurements of α-case can be made for penetration depths that are sufficiently large for micro indentations and weight gains due to oxygen enrichment are significantly high. Structural titanium components are never operated at service conditions that lead to large α-case depths due to the risk of catastrophic failures. Measurement of small α-case depths that form at service conditions are of interest from a design viewpoint. This enables introduction of α-case depth as a design parameter into damage nucleation and growth models for predicting component life under service conditions and developing fail-safe designs. Since the oxidation attack is limited to the outer region of components whereas mechanical properties at elevated temperatures are determined by the bulk cross-section, a promising approach would be to optimize both mechanical properties and oxidation resistance. A quantitative model of α-case depth would be helpful for this purpose. The objective of this study is therefore to quantify α-case depth in

service temperature and time ranges of interest. Experiments were conducted on the most commonly used high temperature titanium alloy Ti-6242. Isothermal oxidation experiments were performed in the temperature range 538–649 °C up to 500 hours, and α-case depth was quantified using metallographic technique.

The material used for the oxidation experiments was a standard Ti-6242 (complete chemical analysis given in Table 1) annealed bar of 25.4 mm diameter supplied by ATI Allvac [11]. Samples of 10×5×5 mm^3 with the 10-mm side along the longitudinal direction of the bar were cut using electrical discharge machining (EDM) and all faces were low stress ground to remove the re-cast layer formed after EDM. Static isothermal oxidation experiments at atmospheric pressure were performed in a laboratory air furnace at 538, 593, and 649 °C. Samples were taken out after 5, 10, 50, 100, and 500 hours of exposure at each temperature. The weight change of each sample after thermal exposure was measured. Samples were then sectioned at mid height, parallel to the furnace contact face. Cut faces of 5×10 mm^2 were metallographically polished and etched by immersing in oxalic tint etchant consisting of 2 mL HF and 98 mL saturated aqueous $C_2H_2O_4$. The tint etch stained the microstructure and revealed interstitial-enriched α-case as a relatively bright layer. The etchant was freshly made in each case and etch conditions were kept constant for all samples. The alpha case region was imaged using optical microscopy. A statistically significant number of measurements of α-case depth in each sample were made along the entire perimeter at approximately 500 μm spacing. The plane of examination included two longitudinal and two transverse sides of the Ti-6242 bar, and the average α-case depth from 60 individual measurements on each sample are reported. Scanning electron microscopy (SEM) was also used to examine microstructures of selected samples. Vickers microhardness measurements were made for verification purpose using a diamond square pyramid indenter and 100 gf load (diagonal lengths of indents in the range 19–25 μm) on 500 h exposed samples.

The starting microstructure of Ti-6242 used in this study, shown in Figure 2, consisted of a bi-modal (mix of equiaxed and lamellar) morphology with primary α volume fraction of 0.47, average primary α grain size of 6 μm, and β phase volume fraction of 0.26. Bi-modal microstructure is typically used for fracture-critical applications to obtain an optimum balance of creep resistance and fatigue resistance [12]. Microstructural features were similar in both the longitudinal and transverse orientations of the bar except that primary α grains were slightly

elongated along the longitudinal orientation. The weight change normalized by the surface area of each specimen after thermal exposure at different temperatures and times is plotted in Figure 3. All samples gained weight in the temperature and time ranges considered. The weight gain increased with increasing time and temperature. The variation of weight gain with time approximately followed a parabolic relationship.

An example of α-case microstructure for the sample exposed at 649 °C for 50 hours, etched with oxalic tint etchant, is shown in Figure 4. Alpha case, consisting of a group of oxygen-enriched α grains, appears as a bright band near the edge of the sample in this micrograph. A montage created by an array of optical micrographs on this sample is included in this figure, which reveals a continuous α-case along the entire periphery of the sample. Alpha case depth was fairly uniform in both the longitudinal and transverse directions. A secondary electron image obtained near the edge of the sample is also shown in Figure 4, which reveals an oxide scale approximately 1 μm thick above the α-case. Oxide scale thickness was in the range 1–3.5 μm for the temperature and time ranges considered in this study. Alpha case could not be distinguished in scanning electron micrographs, either in the secondary or the backscattered electron imaging mode, as sufficient contrast is not created by the higher oxygen concentration in the α-case compared to the base metal. A gradient in oxygen concentration within α-case depth occurs, dropping from the solubility limit to the bulk concentration in the base metal (Figure 1). Shenoy et al. [8] determined that the maximum interstitial solid solubility of oxygen in the α phase of Ti-6242 is about 2.37 wt.% (7 at.%) compared to 14.5 wt.% (34 at.%) in pure α-Ti. Alpha case depth measurements were made based on the assumption that oxalic tint etch contrast captures the entire α-case region. This assumption was verified to be accurate using nano indentation measurements as a function of depth in a similar material [13]. Alpha case microstructures of samples at different temperature-time combinations are compared in Figure 5. Average α-case depth along with standard deviation is plotted against exposure time for each temperature in Figure 6. At 538 °C exposure, α-case depth is small, about 15 μm after 500 h. Above 538 °C, significantly thicker α-case formed. Ten hours exposure at 649 °C resulted in an α-case depth approximately the same as for 500 h exposure at 538 °C. Alpha case depth variation with time at all three temperatures followed parabolic relationships. Microhardness measurements taken on 500 h exposure samples are shown in Figure 7. Microhardness indents were made as close to the edge as possible without cracking the sample. For the sample oxidized at 538 °C, the indent size

was comparable to the depth of α-case. Vickers microhardness of α-case is about 50 points higher than that of the base metal. Microhardness of α-case in the sample exposed at 649 °C was about 100 points higher than that for samples exposed at 538 °C or 593 °C for the same time, which could be due to difference in oxygen concentration in α-case at the location of micro indentation.

Considering the shallow depths of α-case in relation to specimen dimensions, it is reasonable to assume the specimens are of semi-infinite thickness and that approximate solution for Fick's second law of diffusion $x = \sqrt{Dt}$ applies, where x is α-case depth, D is the diffusion coefficient, and t is exposure time. Log-log plots of x vs. t, shown in Figure 8(a), reveal linear trends with excellent correlation coefficients of 0.99. The exponents from these linear fits were close to 0.5. The D values calculated from the best fit lines are plotted against reciprocal of absolute temperatures (T) in Figure 8(b). The D vs. ($1/T$) variation follows an Arrhenius-type relationship, $D = D_o \exp(-\mathrm{Q}/\mathrm{RT})$, where D_o is the pre-exponent factor, Q is the activation energy for diffusion of oxygen in the α phase, and R is the gas constant. From the best fit line, Q was calculated to be 244 kJ/mol. The D values approximated by Shamblen and Redden [7] are also plotted in Figure 8(b), which are about an order magnitude lower than the values obtained in the current study, and the estimated Q was 203 kJ/mol. Differences in D and Q could be attributed to the influence of starting microstructure on diffusion of oxygen in Ti-6242 and errors associated with correlation between microhardness and α-case depth.

In summary, α case depth as a function of time in Ti-6Al-2Sn-4Zr-2Mo alloy follows a parabolic variation in the temperature range 538–649 °C. A drastic increase in α-case depth occurs above 538 °C under static thermal exposure. The activation energy for the diffusion of oxygen in the α phase of Ti-6Al-2Sn-4Zr-2Mo is estimated as 244 kJ/mol in the temperature range 538–649 °C.

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Table 1: Chemical composition of Ti-6Al-2Sn-4Zr-2Mo material used for oxidation study.

Al	Sn	Zr	Mo	Si	Fe	Ni	C	O	N	H	Ti
6.10	1.76	4.16	2.08	0.066	0.048	0.037	0.019	0.132	0.027	0.0051	Bal

Figure Captions

Figure 1. Schematic of oxygen concentration profile in oxidized titanium.

Figure 2. Starting microstructure of Ti-6242 bar (in longitudinal *L* and transverse *T* orientations) used for isothermal oxidation experiments.

Figure 3. Weight change of Ti-6242 samples as a function of time at different temperatures of isothermal exposure.

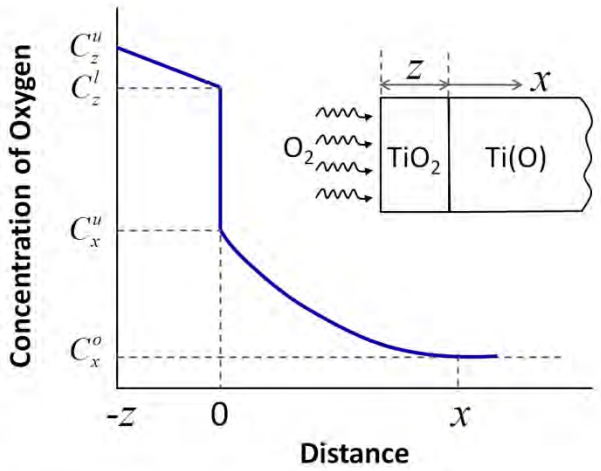
Figure 4. Micrographs of Ti-6242 sample exposed at 649°C for 50 hours revealing subsurface α-case (optical micrographs obtained on oxalic tint etched surface) around the perimeter and oxide scale (secondary electron image) on the surface.

Figure 5. Micrographs of Ti-6242 sample exposed at different temperatures and times comparing α-case depth (optical micrographs obtained on oxalic tint etched surface).

Figure 6. Variation of Ti-6242 α-case depth as a function of time at different temperatures.

Figure 7. Vickers microhardness measurements in the base and α-case regions of Ti-6242 oxidized at different temperatures for 500 hours.

Figure 8. (a) Log-log plot of α-case depth vs. time used for the determination of diffusion coefficients and (b) semi log plot of diffusion coefficient vs. inverse of absolute temperature used for the estimation of activation energy.



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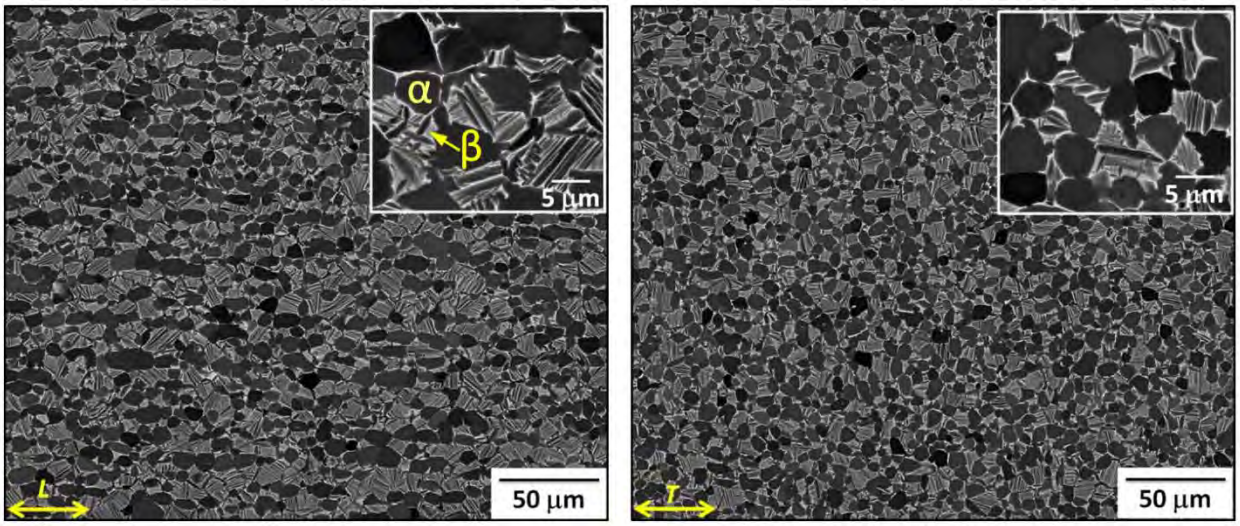
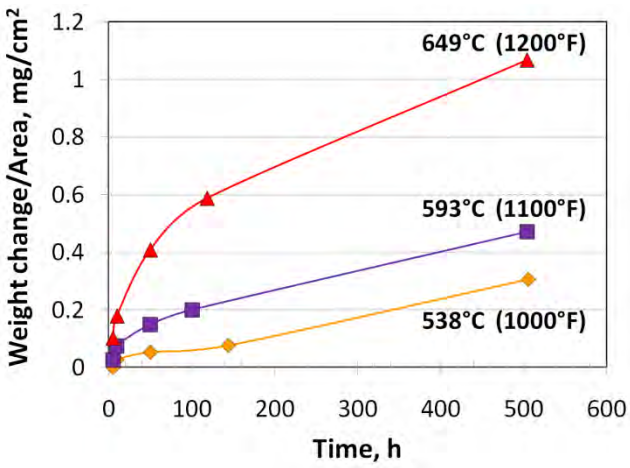


Figure 2. Starting microstructure of Ti-6242 bar (in longitudinal *L* and transverse *T* orientations) used for isothermal oxidation experiments.



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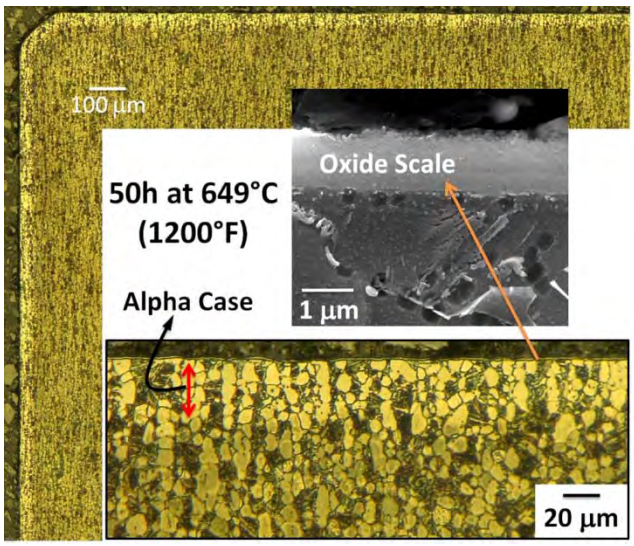

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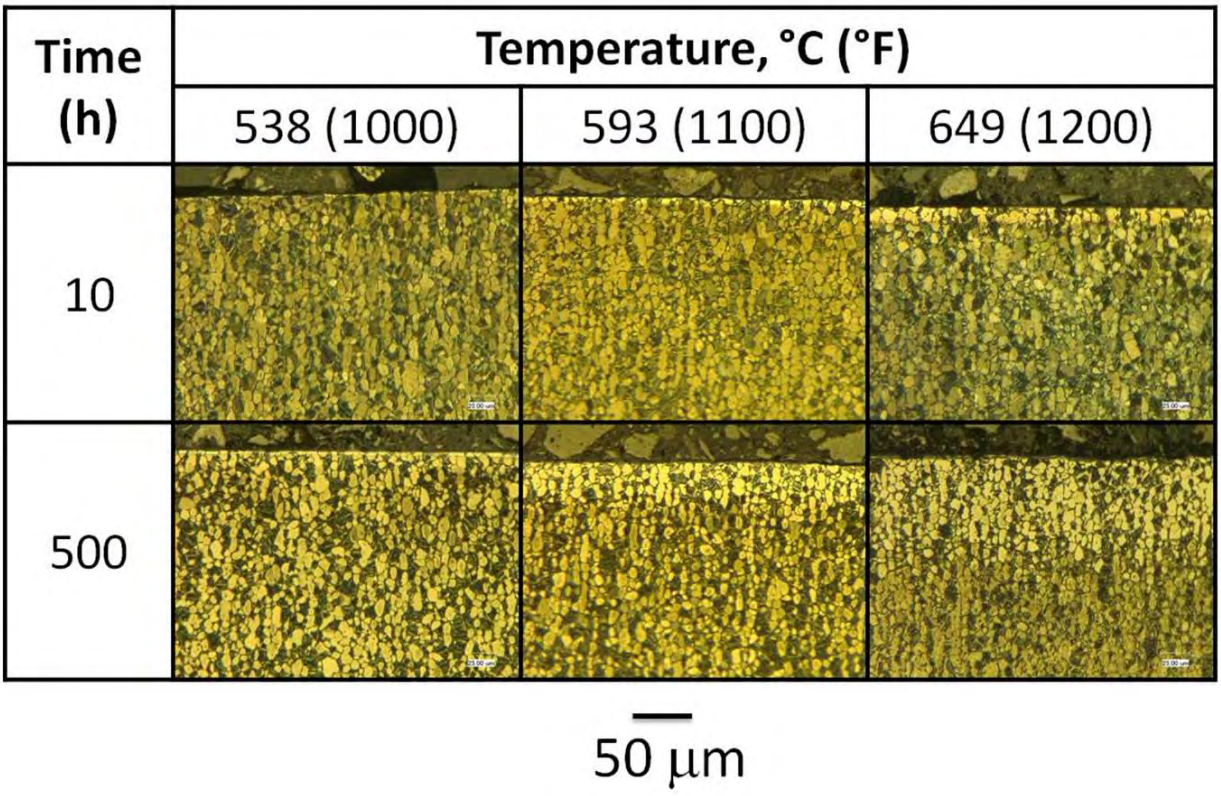

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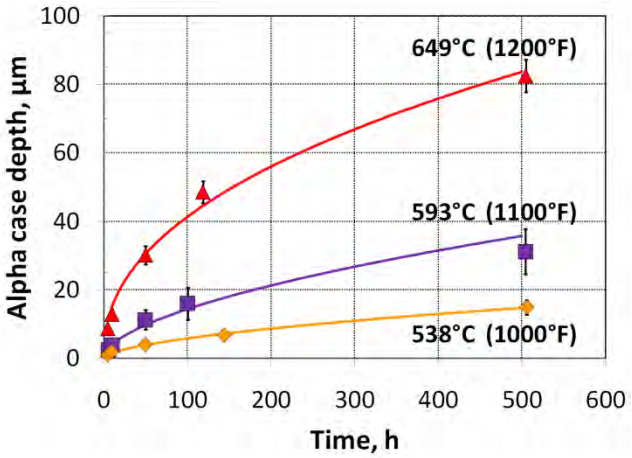
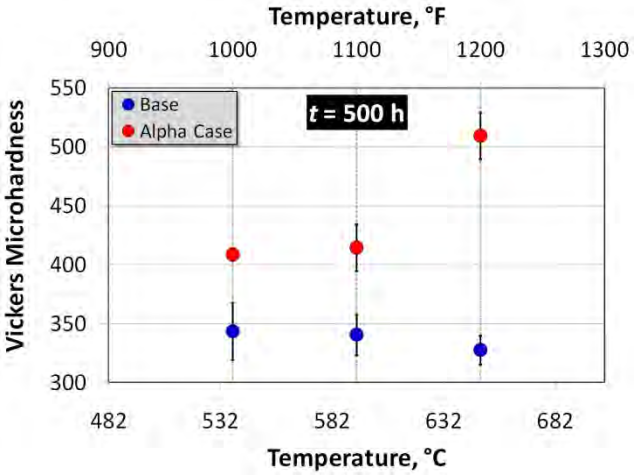


Figure 6. Variation of Ti-6242 α-case depth as a function of time at different temperatures.



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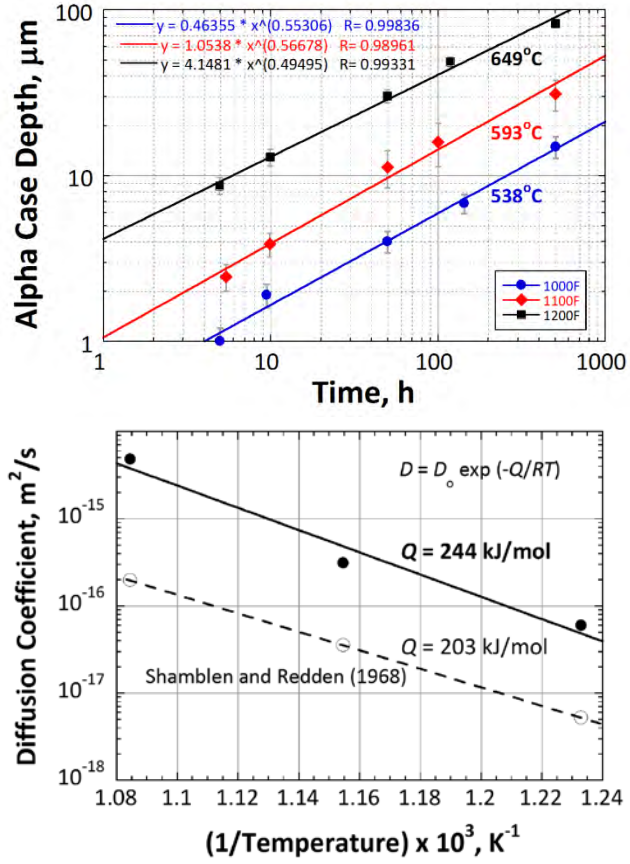

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